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ORIGINAL ARTICLE

An alternative improved method for the homogeneous dispersion of CNTs in Cu matrix for the fabrication of Cu/CNTs composites

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Abstract Copper has a wide range of applications due to its excellent properties (high thermal and electrical conductivity). Carbon nanotubes (CNTs) are widely used as a reinforcing material due to their superior properties. Copper/Carbon nanotube (Cu/CNTs) composites show enhanced mechanical, electrical and thermal properties as compared to pure Cu and Cu composites. Hence, Cu/CNTs composites have tremendous applications. Cu/CNTs are being developed for use as antifungal and antimicrobial agents, which can lead to their further use in biomedical devices and implant materials. The versatility of this material is such that Cu/CNTs are being developed for use in ultra-large scale integrated circuits for use in the latest integrated circuits and semiconductor chips. The composite material is being used as heat sinks for various industries. Cu/CNTs are now also being employed as catalysts for various industrial reactions. Fuel cell electrodes based on Cu/CNTs are being developed to replace expensive Pt/Pd-based electrodes, currently being used. Another application in the energy sector is the use of Cu/CNTs in direct methanol fuel cells and in methanol gas reforming for H_2 production. These extensive applications provided motivation for the current work. However, these applications can only be realized if a stable and uniform Cu/CNTs composite powder can be made. The challenges in fabricating Cu/CNTs composites are: (1) homogeneous dispersion of CNTs in Cu matrix, (2) interfacial bonding between CNTs and Cu matrix and (3) retention of structural integrity of CNTs. Powder metallurgy (PM) has been widely used, but dispersion of Cu/CNTs remains an issue. We employed the molecular level mixing method (MLM), coupled with high energy ball milling (BM) to overcome above mentioned issues. To the best of our knowledge, this is a new process for the homogeneous dispersion of CNTs in copper and has been reported for the first time. To produce a homogenous mixture of Cu and CNTs, a combination of MLM and BM was used in the present work. This method involves using a Cu salt/CNTs mixture in desirable weight ratio (CNTs being were taken in a high concentration), followed by chemical reduction in aqueous medium using $NABH_4$ as reducing agent and EDTA as the oxidation control agent. The resultant mixture (Copper/Carbon nanotube) was mixed with pure Cu using BM. The composites were fabricated using PM, in which the composite powders were first cold pressed at 500–550 MPa followed by sintering at 550–900 °C in a vacuum of 10^{-2} Torr. Characterization was carried out using SEM, XRD and HRTEM, and various mechanical properties were measured using a Universal testing Instron machine.

Keywords Copper/Carbon nanotube composites · Molecular level mixing · High energy ball milling

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Introduction

Copper is a widely used metal and it has a wide range of applications owing to its excellent thermal and electrical properties. In the current age, the requirements of such

materials have increased substantially. This has led to the development of many new composite materials. However, for many applications pure Cu cannot be used because of its lower strength. Therefore, improvement in the properties of copper has become essential for its applications in cutting-edge technological applications. Copper nanoparticles are used today in many fields: electrode materials (Li and Fu 2008), catalysts (Lambert et al. 2007), electronics (Liu and Bando 2003), nanofluids (Garg et al. 2008), and gas sensors (Valentini et al. 2007). Copper at the nanoscale becomes more useful, this is due to the fact that copper nanoparticles have high surface area and small size. The improvement of mechanical properties of copper is important for its use in a larger number of fields. Carbon nanotubes (CNTs), since their discovery (Iijima 1991), have been used as a reinforcement material for the fabrication of a variety of composites. The mechanical properties of functional copper materials are greatly hindered by alloying with other metals. CNTs in this case provide a new avenue for the reinforcement of copper matrix-based materials; they not only help in retaining the properties of copper matrix, but also enhance the mechanical properties of copper (Cha et al. 2005). A functional composite of Cu/CNTs would be highly desirable. Cu/CNTs exhibit enhanced thermal and electrical properties allowing them to be employed in latest semiconductor chips, as transistors are extremely close to each other requiring effective thermal dissipation, also due to higher electrical conductivity than pure copper narrower channels for integrated circuits and semiconductor chips can be made leading to further reduction in size (Liu et al. 2008). Cu/CNTs-based materials are being used for anti-microbial and anti-fungal applications (Ruparelia et al. 2008) due to their activity against bacteria resistant to common antibiotics, which could lead to their further use in water filtration, air purification and antibacterial packaging. Nanofluids based on Cu/CNTs/Carbon nanoparticles are being employed as thermal management systems (Liu et al. 2011) in various industries and as direct solar energy absorbers (Han et al. 2011). It is a field of active research. The key factor in the synthesis of a suitable Cu/CNTs composite is effective dispersion of CNTs in the Copper matrix due to the large difference in densities (Cu = 8.9 g cc^{-1} and CNTs = 1.4 g cc^{-1}). Currently two main methods are pursued for the synthesis of Cu/CNTs composites viz. Molecular level mixing (Cha et al. 2005; Kim et al. 2008; Jeong et al. 2007) or Powder metallurgy (Pham et al. 2011; Kim et al. 2009; chu et al. 2010). In this work we have studied both methods of preparation. Ball milling is not efficient in producing homogeneous dispersions of CNTs in Cu matrix, molecular level mixing is a better choice as it produces a highly homogeneous dispersion of Cu/CNTs. Molecular level mixing (Cha et al. 2005), does not result in the production of Cu/CNTs, but a high amount of CuO/Cu_2O is achieved, a further step requiring reduction in H_2 at 400 °C is required. We have overcome this problem to a decent level with the use of oxidation control agent Ethylenediammine tetraacetic acid (EDTA). EDTA is a chelating agent, which forms a complex with the metal ions and prevents their oxidation in liquid. In the current method Cu precursors were reduced in the presence of a high concentration of CNTs in aqueous medium. Filtration is required as aqueous medium is mostly employed for the progress of molecular level mixing, and unwanted substances are removed in the process. In the current study, we aimed to address all these issues and have hence derived a hybrid method using both ball milling and molecular level mixing. The novelty of the current work lies in the method of dispersion of CNTs in the Cu matrix. An in situ process was used for depositing Cu nanoparticles on functionalized CNTs. The concentration of CNTs is higher to that of Cu nanoparticles. In a way, the Cu nanoparticles are employed as a wetting agent. These modified CNTs were then used for high energy ball milling with Cu powder for the formation of Cu/CNTs composite powder. CNTs modified by this process show a high level of dispersion in the Cu matrix and better interfacial bonding resulting in improved mechanical properties.

Experimental

Materials and methods

All chemicals were purchased from Fisher Scientific (India); Carbon nanotubes were purchased from Nanocyl, Belgium, all chemicals were of analytical grade.

Functionalization of carbon nanotubes

Functionalization of carbon nanotubes is essential in the preparation of Cu/CNTs nanocomposite materials. Functionalization can be achieved by a number of methods; ball milling (Ma et al. 2009), plasma (Naseh et al. 2010) and acid (Xia et al. 2009). We used the acid functionalization route. Multiwalled carbon nanotubes were refluxed in an acidic solution containing H_2SO_4 and HNO_3 in 3:1 ratio, 50 % acid concentration. CNTs were refluxed at 80 °C for 10 h. CNTs were then filtered and washed repeatedly with ethanol and distilled water. Drying of CNTs was carried out in a vacuum oven at 80 °C for 4 h.

Introduction of carboxyl group is observed on the CNTs and it acts as a point for bonding between metal matrix and CNTs. Van der Waal's forces of the CNTs are overcome by the presence of carboxyl and hydroxyl groups preventing agglomeration of CNTs.

Modified molecular level mixing

$CuSO_4$ was used as the precursor material for production of nanoscale composites. $NaBH_4$ was used as the reducing agent. EDTA was employed as oxidation control agent. Sodium dodecyl sulphate (SDS) was used as a surfactant to ensure dispersion of CNTs in aqueous medium. NaOH is used to maintain the pH of the solution between 10 and 11, and ensures the progress of reaction at a suitable speed. $CuSO_4$ was added to distilled water along with NaOH and EDTA, under magnetic stirring and a temperature of 40 °C was maintained. A blue solution was obtained. CNTs were added to the solution and SDS was added to ensure homogeneous dispersion. $NaBH_4$ was added for the reduction of $CuSO_4$ and production of nanoscale particles of copper. Addition of $NaBH_4$ causes transformation of blue to dark red colour indicating the formation of copper nanoparticles. Materials were used in the following concentrations 1 M EDTA, 0.02 M $CuSO_4$, 0.1 M NaOH, 0.25 M $NaBH_4$. CNTs were taken in a very high concentration. We exploited the molecular level mixing method (MLM) for the formation of Cu coated CNTs. Filtration followed by drying in vacuum oven at 80 °C for 8 h was done to obtain copper coated CNTs powder.

This is the essential difference between MLM and our method. Cu nanoparticles on the surface of the CNTs act as an innovative wetting agent. The phase mismatch between CNTs and Cu is reduced and the formation of Cu/CNTs is made easier. In a sense, we have reversed the MLM and controlled the oxidation to prevent the formation of excessive copper oxides species.

Ball milling

Copper powder was ball milled for 10 h at 500 rpm using stainless steel balls; smaller diameter balls (5 mm) were used to increase the contact area between copper powder and balls for better milling. Ball to powder ratio was maintained constant at 10:1. Ethanol was taken as a process control reagent to avoid cold annealing of the material while milling. Ball milling decreases the particle size of the powder. Another important feature of ball milling is that it leads to grain refinement which is an important aspect in improving the interface between metal matrix and CNTs.

Synthesis of Cu/CNTs composite powder

Copper coated CNTs produced from modified MLM were milled together with previously milled Cu powder. Milling was done using stainless steel balls and the ball:powder ratio was kept constant at 10:1. Milling was done for 5 h at 250 rpm. Ethanol was taken as a process control reagent to avoid cold annealing of metal. Milling was done at milder conditions compared to other reported methods to prevent CNTs damage, which renders their reinforcing properties. Cu/CNTs powders were prepared with different concentration of CNTs varied from 0.5 to 1.5 wt% CNTs.

Hence, a hybrid method was used to combine ball milling and molecular level mixing, addressing issues of both methods. Copper oxide species were minimized with the help of EDTA. A large amount of Cu/CNTs composite materials can be produced by this method.

Formation of Cu/CNTs composites

Cu/CNTs composites of various shapes and sizes, as recommended in ASTM standard, were fabricated by cold pressing the Cu/CNTs composite powder at 550 MPa, followed by sintering at 900 °C for 4 h under vacuum of 10^{-2} Torr. Composites of various shapes and sizes were fabricated to measure the microhardness, compressive and bending strength.

Instrumentation

Scanning electron microscope (SEM, model LEO 440) was used to study the microstructure of the composite. Microhardness was tested using Zwick 3212 microhardness tester. Universal testing Instron machine (Instron model 4041) was used to study mechanical properties of the composites. Ball milling was done on Retsch PM 100 machine. X-ray diffraction tests were performed at room temperature on a Rigaku MiniFlex^{TM} II system using CuKα radiation ($\lambda = 0.15418$). Fourier Transformation Infra Red spectroscopy of acid functionalized CNTs was done using Perkin Elmer series spectrophotometer. Thermal conductivity tests were carried out using Unitherm series thermal analyzer. A high resolution transmission electron microscope (HRTEM, model FEI Tecnai G2 F30 STWIN with FEG source at the electron acceleration voltage of 300 kV) was used to study the dispersion of CNTs in Cu matrix.

Results and discussion

Characterization of CNTs

Figure 1a shows FTIR spectra for acid treated CNTs and Fig. 1b, FT-IR spectra for pure carbon nanotubes. It can be seen that there is a modification of the spectra after acid treatment. Acid treated CNTs show extra peaks at 1,110 and 1,720 cm^{-1}, which are assigned to C-O-C and carbonyl group (C=O), hydroxyl group peak is at 3,400 cm^{-1}. Functionalization is an essential part for the formation of the composite, as the functional groups provide a point of bonding between metal surface and the CNTs.

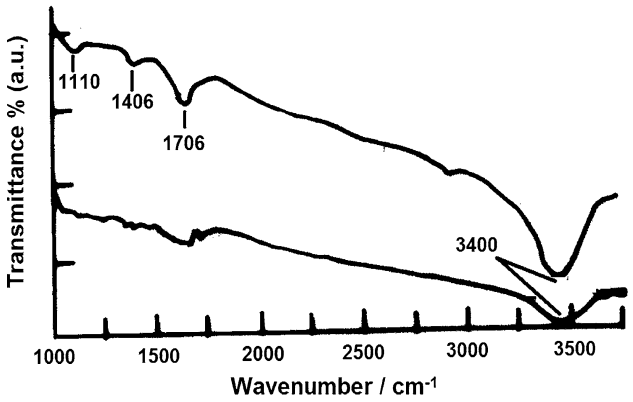

Fig. 1 FT-IR spectrum of **a** acid treated CNTs and **b** pure CNTs

X-ray diffraction of Cu/CNTs composite

Figure 2a shows the XRD data obtained when 0.1 M EDTA is used, as can be seen from the figure, large amount of Cu_2O is obtained due to the oxidation of copper nanoparticles as soon as they are formed. Nanoparticles are much more prone to oxidation as they are more reactive than their bulk counterparts owing to small size and higher surface area. Figure 2b shows the data obtained from using 1 M EDTA, the oxidized species are nearly absent and hence the role of EDTA can be established as oxidation control agent, and successful synthesis of Cu nanoparticles coated CNTs is observed. Figure 2c shows the final composition of Cu/CNTs composite obtained after ball milling, the CNTs concentration is reduced to 0.5–1.5 wt% and hence has to be shown in inset. For CNTs, generally the peak associated with the (002) diffraction is located at 26.0°. Copper nanoparticles show characteristic peaks at 43.2°, 50.4° and 73.2° corresponding to the fcc phase of copper. Copper oxide peak is seen at 36.5°. XRD data are helpful in establishing the successful synthesis of Cu/CNTs composite material and elucidates the role of EDTA.

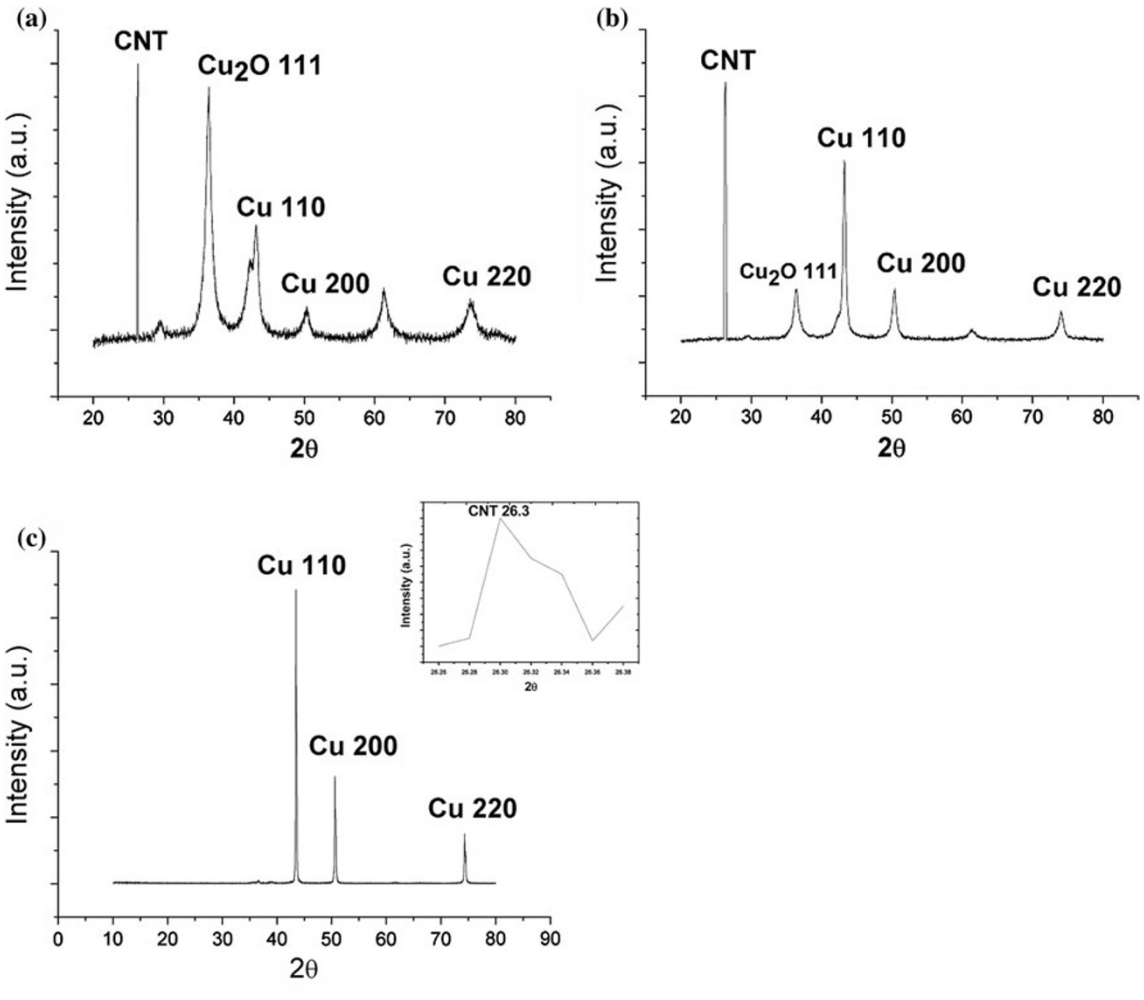

Fig. 2 XRD data for **a** Cu/CNTs prepared using 0.1 M EDTA **b** Cu/CNTs prepared by using 1 M EDTA and **c** final composition of Cu/CNTs after ball milling

Microstructural analysis of Cu/CNTs composite powder and dispersion of CNTs in Cu matrix

Microstructure analysis and the dispersion of acid functionalized CNTs in Cu matrix were studied using SEM and HRTEM. Figure 3a shows the SEM image of Cu/CNTs composite powder produced by ball milling. Agglomeration of CNTs can be seen at one site, this indicates that there is minimal dispersion of the CNTs, hence, it is ascertained that ball milling alone is not sufficient to produce highly dispersed systems of Cu/CNTs composite powder. Figure 3b shows the results obtained using molecular level mixing; CNTs can be seen dispersed in a highly homogeneous method with the copper matrix, CNTs are not agglomerated at one site, this establishes the superiority of MLM over the ball milling method in producing homogeneously dispersed Cu/CNTs powders. Also there is no damage to the CNTs when being processed by molecular level mixing. Figure 3c depicts the results of molecular level mixing combined with ball milling which is the main focus of this work. It can be seen that this method is also capable of producing homogeneous Cu/CNTs composite powders, carbon nanotubes can be seen coating the copper particles. Bulk production of Cu/CNTs powders is possible with this method. SEM micrographs establish the dispersion and hence overall quality of the Cu/CNTs powder.

Figure 4 shows the HRTEM results confirming the homogeneous distribution of CNTs in the Cu matrix. CNTs can be seen as separate entities; they are not tangled and agglomerated with each other. Particle size of copper nanoparticles can be estimated to be between 20 and 50 nm. Combination of SEM and HRTEM images illustrates the high dispersion level attained by the current method.

Mechanical properties of Cu/CNTs composites

Microhardness tests were done in accordance with ASTM standard E-384. Compressive strength specimens were prepared as recommended by ASTM E9 standard. For compressive tests, cylindrical samples of length 9 mm and diameter 6 mm were made. Three point bending strength specimens were prepared as per ASTM standard E399-90S.

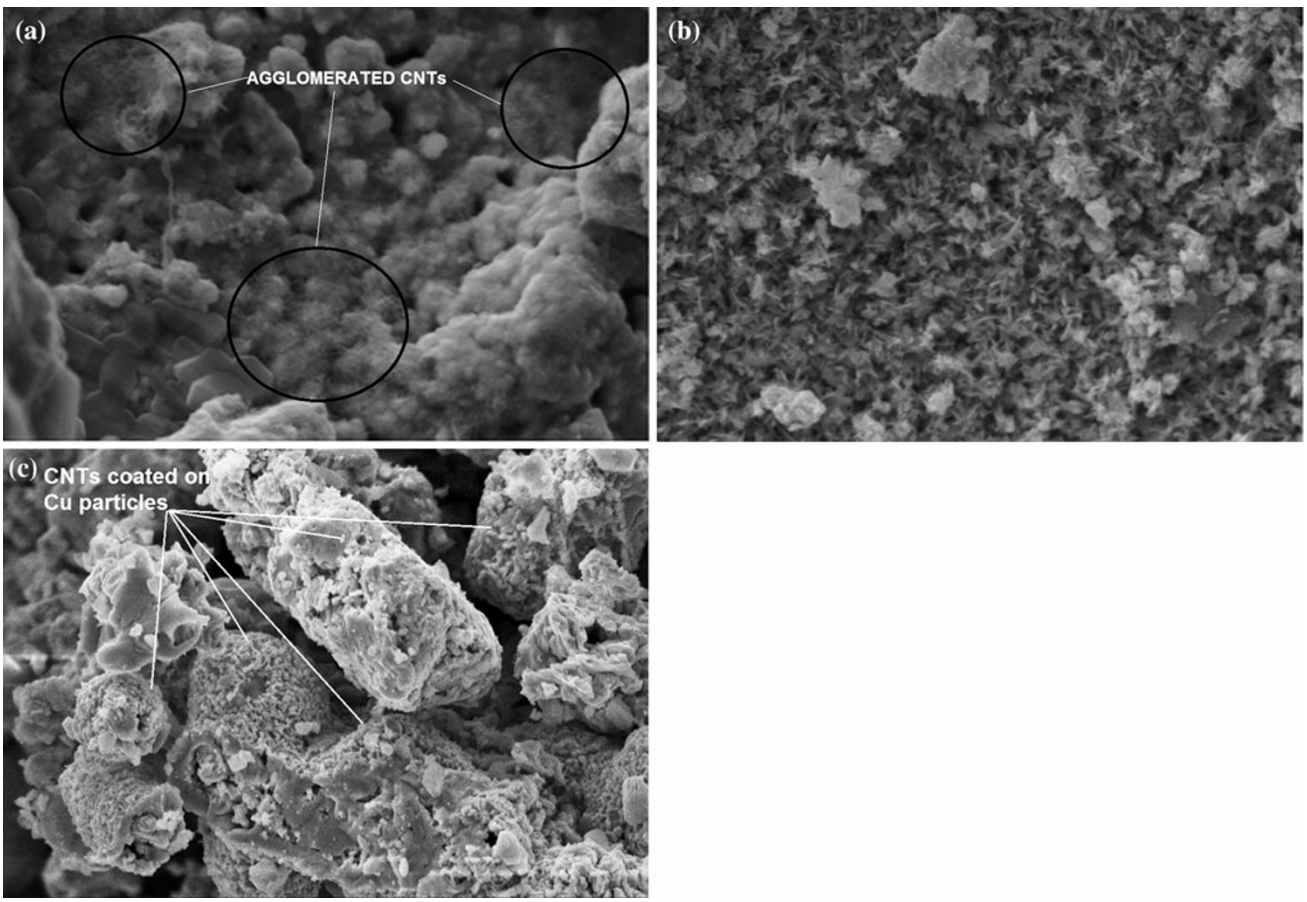

Fig. 3 Scanning electron micrograph of **a** Cu/CNTs prepared by ball milling **b** Cu/CNTs prepared by molecular level mixing and **c** Cu/CNTs prepared by a combination of molecular level mixing and high energy ball milling

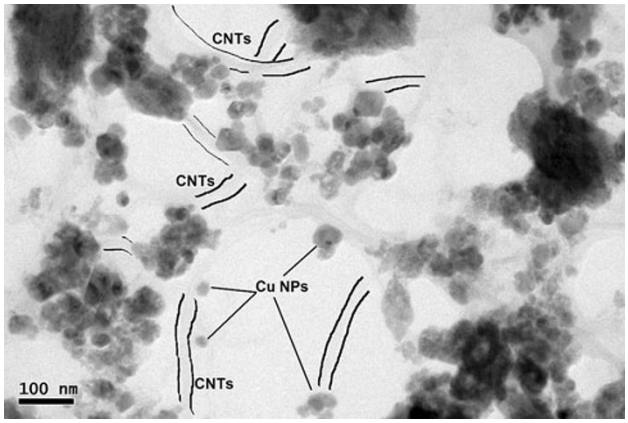

Fig. 4 HRTEM micrograph of Cu/CNTs prepared by molecular level mixing and high energy ball milling

At least 10 sets of results were obtained for each test to confirm repeatability of the results. All specimens were rubbed with a fine diamond paste to make the surfaces smooth before tests. Dry lubricants are applied to the composites before compressive tests are done to ensure minimal friction, avoiding any discrepancies in the results. The flexural strength was calculated using the formula $3FL/2bd^2$. Where, $F =$ Load at the fracture point in Newton, $L =$ Length of support span, $b =$ width and $d =$ thickness of the specimen.

The mechanical properties of Cu/CNTs composites fabricated in the present work are shown in Table 1. The mechanical properties of Cu increase on the addition of carbon nanotubes, because of the load sharing between Cu matrix and carbon nanotubes. CNTs can withstand much higher loads than copper matrix and hence there is a substantial increase in the mechanical properties of carbon nanotubes. Another important factor is the interfacial bonding between the CNTs and Cu matrix, which is aided by the functionalization of CNTs, introduction of carboxyl and hydroxyl groups on the surface of the carbon nanotubes provides a binding site for the metal matrix to the CNTs, which are inert otherwise. Homogeneous dispersion may be the most important factor. If CNTs agglomerate at one site then that area will receive the maximum load and hence formation of cracks will be seen at that point, also the rest of the composite will not be able to withstand heavy loads due to the lack of load transfer to carbon nanotubes and the whole structure will collapse. It is, therefore, extremely important to have a highly dispersed system so that load sharing is done in an even manner minimizing the load in a single area dispersing the load evenly and hence increasing the total load/force that a composite can withstand. These properties have not been reported in most of the works that have been carried out till date.

Table 1 Mechanical properties of Cu/CNTs composites with varying CNTs concentration

Composite material	Microhardness (Hv) (kg/mm^2)	Compressive strength (MPa)	Flexural strength (MPa)
Cu pure	54	275	190
Cu/CNTs (0.5 wt% CNTs)	92	350	215
Cu/CNTs (1.0 wt% CNTs)	111	521	255
Cu/CNTs (1.5 wt% CNTs)	127	633	307

Thermal conductivity

The thermal conductivity of the Cu/CNTs composite produced by molecular level mixing is observed to be lower than that of pure copper, around 250 W/mK (Kim et al. 2011), compared to 394 W/mK of pure copper. The interfacial bonding between CNTs and Cu matrix needs further work (Kim et al. 2011). CNTs and Cu interfacial region is said to act as a thermal barrier with minimal thermal conductivity and further work is needed in this area (Kim et al. 2011). We have obtained thermal conductivity of 424 W/mk for Cu/CNTs 1.5 wt%. This was the highest value attained in the current work. This high value was not repeatable for all samples at 1.5 wt%. The thermal conductivity obtained for other composites was in the range of already reported work between 230 and 250 W/mK. Much more work is, therefore, needed in this direction. It is observed from this work that the processing conditions of the composite materials also play a role in the final thermal conductivity. A much detailed study is required to fully understand all aspects of thermal conductivities of this composite material.

Conclusion

The need for employing this novel hybrid method is justified by the results. The high level of dispersion leading to better interfacial bonding between Cu matrix and CNTs can be achieved as seen through the SEM and HRTEM results. The increased mechanical properties of Cu/CNTs over pure Cu and compared to previously reported works shows that the current method has a distinct advantage over other methods employed for the synthesis of Cu/CNTs. The high compressive strength can be attributed to the high ductility of copper. CNTs are a very stiff material, yet they did not pose any hindrance to ductility of Cu as they have been dispersed homogeneously, and Cu-CNTs interface is optimal due to the modification of CNTs with Cu nanoparticles. Another aspect of this method is that it does not involve any drastic conditions and processing is carried out at room temperature. Therefore, we can conclude that this

method can be scaled-up for possible commercial production of Cu/CNTs composite materials. The composite powder can be processed in any way for various applications after its production. This method could be applied to the synthesis of Cu/CNTs, using SWCNTS and DWCNTs to see if the mechanical properties show further improvement. As this composite has a lot of applications, the use of this composite can be tested for various applications, which will give us a better understanding of the material.

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